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Safe and performant electrolytes for supercapacitor. Investigation of esters/carbonate mixtures

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HIGHLIGHTS

- Electrolytes involving functional acetate as co-solvent exhibit high performances for supercapacitor application.
- Safe electrolytes can be obtained displaying high conductivities in a large temperature range.
- Longer cycle life should be reached using Spiro-(1,1′)-bipyrrolidiniumBF_4 along with the improvement at low temperature.

ARTICLE INFO

ABSTRACT

This paper details the influence of adding ester co-solvent to ethylene carbonate (EC) based electrolyte in the view of supercapacitor applications. The incorporation of ester solvents with methoxy or fluorinated groups allows a good compromise to be reached between electrochemical performance in a wide temperature range and safety issue. The use of spiro-(1,1′)-bipyrrolidinium tetrafluoroborate ($SBPBF_4$) instead of tetraethylammonium tetrafluoroborate ($TEABF_4$) allows the increase of electrolyte conductivity at low temperature thanks to its higher solubility. An improvement of capacitance stability is also obtained with the use of $SBPBF_4$.

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1. Introduction

The electrical double-layer capacitors (EDLCs) or supercapacitors are energy storage systems [1,2] which may be used in portable devices, hybrid vehicles and storage of the energy generated by solar cells [3,4]. The electrical charge is stored in the electrical double-layer formed at the electrode/electrolyte interface. Thus, this technology presents high power density, long cycle life, high efficiency, wide range of operating temperature, environmental friendliness, and safety. As the energy stored in capacitors is proportional to the square of voltage, organic electrolyte supercapacitors represent an interesting choice due to their wider potential window compared to aqueous electrolyte capacitors. Most of EDLC researches are dedicated to the preparation of carbon materials and to the studies of their performances as electrode material. Surprisingly very few papers are devoted to the comparison of electrolyte performances [5–11]. The main impact of electrolyte conductivity and electrochemical stability is on supercapacitor constant time, nominal voltage and cycle life. The common organic solvents used for EDLCs are acetonitrile (ACN), and propylene carbonate (PC). Acetonitrile based electrolytes present high electrochemical stability and high conductivities even at low temperature, due to the low viscosity of ACN and its high dielectric constant ($\varepsilon = 38$). However, it is a flammable and harmful liquid, thus supercapacitors based on acetonitrile electrolyte set some security problems. Taking into

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account this safety issue, irritant and non-flammable PC is also involved in EDLC. Nevertheless, poor conductivity performances were obtained, especially at low temperature due to the high viscosity of this solvent. In this context, others solvents have been also investigated, such as γ-butyrolactone [7], dimethylketone [7], sulfolane [11], methoxyacetonitrile [5] and methoxypropionitrile [5]. Methoxyacetonitrile and methoxypropionitrile permit to reach interesting conductivity values [5], with solvents with flash point higher than 30 °C. The conductivities obtained with γ-butyrolactone and sulfolane are lower, due to their higher viscosity; this could be offset by a large electrochemical stability allowing the increase of the supercapacitor operational voltage. However, while many studies were devoted to the optimization of the lithium-ion battery electrolyte, using solvent mixtures, such studies have been rarely described on supercapacitors in the literature. M.S. Ding et al. [12] observed an increase of the electrolyte electrochemical stability and a decrease of the solidification temperature with the addition of γ-butyrolactone to ACN based electrolytes. The incorporation of ethyl acetate or methyl acetate in ethylene carbonate (EC)/trimethylethylammonium tetrafluoroborate based electrolytes allows higher ionic conductivity to be obtained at low temperature. These systems also exhibited a pseudo-capacitive behaviour for a cell voltage <3 V, associated to the electrolyte electrochemical stability [9,10]. However the esters used suffer from a low flash point and high volatility, which may be detrimental to security issues.

With a view to optimizing the performances, the influence of the nature of the ammonium salt has also been investigated in literature. The most common salt is tetraethylammonium tetrafluoroborate (TEABF$_4$). This salt exhibits good electrochemical stability, a low price but a limited solubility in solvents of intermediate (/moderate) polarity. In order to increase the salt solubility, others salts were investigated [13,14]. Due to the ammonium dissymmetry, the triethylmethylammonium tetrafluoroborate allows the increase of the solubility limit without being detrimental towards the electrochemical stability and ionic conductivity [15].

The aim of this paper is to propose the use of ester solvents as co-solvent in EC based electrolytes. The addition of ester co-solvent should enable to exhibit a good compromise between electrochemical performances in a wide temperature range and security issues. Two salts were investigated: the common TEABF$_4$, and the spiro-(1,1′)-bipyrrolidinium tetrafluoroborate (SBPBF$_4$) (Scheme 1), which is more soluble in a large variety of solvent mixtures [16].

2. Experimental section

2.1. Thermal measurements

DSC tests were performed using a TA Instrument DSC 2920 CE. Samples of 3 mg were sealed in aluminium pans in a glove box. Each sample was heated from −100 °C to 40 °C and cooled down from 40 °C up to −100 °C at a rate of 5 °C min^{-1}. The melting and crystallization temperatures, T_m and T_c were determined at the top of melting and crystallization peaks respectively.

2.2. Viscosity

The viscosity was measured on a capillary viscometer. The kinematic viscosity is obtained as the average of 10 measurements with an accuracy of 1%. The dynamic viscosities were calculated by the formula $\eta = K \rho t$ where K, ρ and t are the viscometer constant (0.01032 mm^2 s^{-2}), the density of the electrolyte (g cm^{-3}) determined at 40 °C and the time of electrolyte flowing through the capillary (s) respectively.
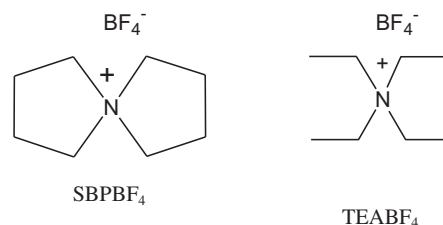
Scheme 1.

2.3. Electrochemical investigations

Conductivities were determined by electrochemical impedance spectroscopy using an HP 4192A Impedance Analyser in the frequency range 5 Hz–13 MHz. The samples were placed in a dip-type glass cell with two Pt electrodes at a constant distance and measurements were performed from −30 °C to 70 °C under argon. The temperature was equilibrated for 1 h before each measurement. The conductivity, for the same electrolyte is determined twice in two different conductivity cells to check the reproducibility of measurements (uncertainties of conductivity values are estimated to be ±0.3 mS cm^{-1}). The cell constant was determined by using a 0.1 M KCl solution.

Cyclic voltammograms (CV) were recorded at room temperature in a glove box. The counter electrode was a Pt wire, and the working electrode was Pt or a glassy carbon with a diameter of 3 mm. The scan rate used was 10 mV s^{-1}. The reference electrode was an Ag wire in 10 mM AgNO$_3$ in acetonitrile +0.1 M tetrabutylammoniumBF$_4$. Potential can be converted to the NHE scale by adding 0.542 V [17]. The anodic and cathodic limits were defined as the potential at which the current density is equal to 0.3 mA cm^{-2}. Due to the low solubility of TEABF$_4$ in medium polarity solvents, their electrochemical stability was evaluated as molar concentration in ACN + TEABF$_4$ 1 M electrolytes. All the solvents studied were distilled under argon or vacuum and stored in a glove box. The ACN + TEABF$_4$ 1 M electrolyte exhibits a large electrochemical stability, with oxidation and reduction potentials at 2.6 V vs Ag/Ag$^+$ and −2.4 V vs Ag/Ag$^+$ respectively. These limits in potential were associated, in the studies, to the oxidation and reduction of the BF$_4^-$ anion [18,19].

For EDLC investigation, the electrode was supplied by Batscap. These electrodes contain 10% of PVDF and 10% of conductive additives; the carbon charge loading is equal to 2.94 mg per cm^{-2}. Previous experiments have demonstrated that these chemicals do not affect electrolyte stability (or have a minor effect). The electrodes were dried several days at 100 °C in vacuum and then stored in a glove box. The electrochemical cell was assembled in a Swagelok configuration using 1.13 cm^2 surface electrodes. Cyclic voltammetry was performed in a two electrode system (i.e. two identical carbon electrodes separated by a cellulose based separator (25 μm, >70% of porosity)) at 100 mV s^{-1} and 1 mV s^{-1} at 20 °C. We have demonstrated that separator changes do not strongly improve electrochemical performance of electrolyte. Galvanostatic cycling was performed using a current density of ±9 mA cm^{-2}, with an operating voltage from 0 V to 2.3 V. The time constant of the system was determined using the "IR" drop at the initial portion of the discharge curve during the galvanostatic charge/discharge investigation.

2.4. NMR measurements

NMR measurements were carried out on 9.4 T Bruker Avance 400 NMR spectrometer equipped with a Bruker 5 mm dual broadband/{^{1}H–^{19}F} probe with a z-axis and a temperature

controller (stability and accuracy ±0.2 °C). NMR resonance frequencies are 400.13 MHz and 376.50 MHz for ^{1}H and ^{19}F, respectively.

The self-diffusion measurements were performed with the pulsed field gradient stimulated echo and LED sequence using 2 spoil gradients (PFG NMR) [20]. The magnitude of the pulsed field gradient was varied between 0 and 40 G cm^{-1}, the diffusion time, Δ, between two pulses was fixed at 100 ms and the gradient pulse duration, δ, was set between 3 ms and 18 ms, depending on the diffusion coefficient of mobile species, D. This allowed to observe the attenuation of spin echo amplitude over a range of at least 2 decades leading to good accuracy ($<$5%) of the self-diffusion coefficient values. They were determined from the relationship ln (I/I_0) $= -Dg^2 \gamma^2 \delta^2(\Delta - \delta/3)$, where g is the magnitude of the two gradient pulses, γ is the gyromagnetic ratio of the nucleus under study and I and I_0 are respectively the area of the signal obtained with or without gradient pulses, D the diffusion coefficient, δ the gradient pulse duration and Δ the diffusion time.
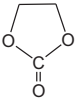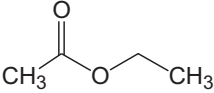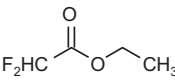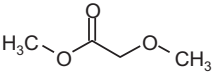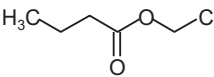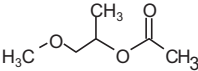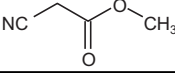
3. Results and discussion

An electrolyte for supercapacitor has to exhibit a good ionic conductivity, high electrochemical stability and thermal stability. Ethyl acetate (EA) is a very low viscous solvent, which is used in lithium battery technology, in addition to carbonate based solvents, to improve the ionic conductivity at low temperature. Furthermore, the ester exhibits high electrochemical stability in presence of TEABF$_4$, from 2.3 V vs Ag/Ag$^+$ in oxidation up to -2.4 V vs Ag/Ag$^+$ in reduction, presumably due to the reduction of BF$_4^-$ anion. The drawback of EA is its high volatility, weak polarity and high flammability with a flash point of -3 °C.

In order to increase the flash point and the polarity without compromising the viscosity, ester solvents with functional groups i.e. methoxy, nitrile, halogen in the shorter alkyl moiety groups were evaluated. The physicochemical properties of the studied solvents are reported in Table 1. All the selected solvents exhibit a flash point higher than 25 °C, thus much higher than EA and ACN. The replacement of CH$_3$ by a polar group such as nitrile or methoxy increases significantly the flash point and the dielectric constant. This is well illustrated by the comparison of methyl cyanoacetate (MCA) and methyl propionate (MPO), which exhibit $F_p = 43$ °C and $\varepsilon_r = 29.3$ for MCA instead of $F_p = 6$ °C and $\varepsilon_r = 5.4$ for MPO. The same trend is observed comparing methoxyethylacetate ($F_p = 45$ °C and $\varepsilon_r = 8.25$) and propyl acetate ($F_p = 10$ °C and $\varepsilon_r = 6$). The replacement of CH$_3$ by Cl leads also to significant effect, since chloromethyl butyrate (ClMB) shows $F_p = 55$ °C and $\varepsilon_r = 9.51$ instead of $F_p = 26$ °C and $\varepsilon_r = 5.8$ for ethyl butyrate. The replacement of CH$_3$ by F has a moderate effect. Indeed, fluoropentane exhibits $F_p = -12$ °C and $\varepsilon = 4.24$ instead of $F_p = -22$ °C and $\varepsilon_r = 2$ for hexane.

3.1. Electrochemical investigation

Although the chemical modification of the ester induces an increase of the flash point, this should be not detrimental to its redox stability. Electrochemical windows of the solvents were determined by cyclic voltammetry on a platinum electrode. The voltammograms obtained with ester solvents with a polar group are given in Figs. 1 and 2. The oxidation of ClMB occurs at the same potential as EA, while ethyl difluoro acetate (EDFA) exhibits higher kinetic stability towards oxidation. Regarding the cathodic part (Fig. 2), the reduction of ClMB is observed close to -0.4 V vs Ag/Ag$^+$. This reduction wall is presumably due to the weak stability of the C—Cl bound. The reduction process involves the release of Cl$^-$ anion and the formation of an unstable anion radical [24]. This behaviour

Table 1
Flash point, viscosity and dielectric constant of solvents.

Solvent	Formula	F_P/°C	η/mPa s at 40 °C	ε_r
EC		143[a]	1.96[e]	90 (40)[g]
Ethyl acetate (EA)		-3[a]	0.34[e]	6 (20)[g]
Ethyl difluoro acetate (EDFA)		25[b]	0.65[e]	–
Methylmethoxyacetate (MMOA)		35[a]	0.82[e]	–
Chloromethylbutyrate (ClMB)		55[c]	–	9.51 (30)[g]
Methoxy-2-propyl acetate (MPA)		43[a]	0.88[e]	7.6 (30)[f]
Methyl cyanoacetate (MCA)		43[d]	3.82 (50)[f]	28 (20)[h]

Temperature is indicated in bracket. Physical properties are cited for Fp from Material Safety Data Sheet from:
[a] Aldrich.
[b] Rhodia.
[c] Acros.
[d] Science Lab.
[e] For η: our data.
[f] Ref. [21].
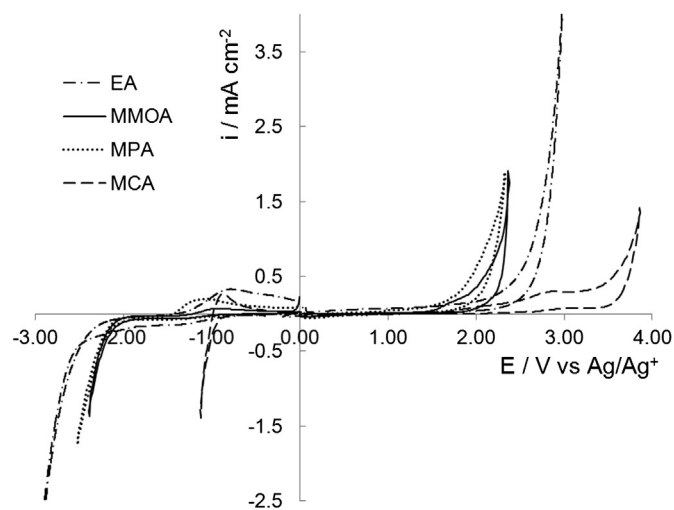[g] For ε_r: Ref. [22].
[h] Ref. [23].

Fig. 1. Cyclic voltammograms in the anodic and cathodic regions for EA, MMOA, MPA and MCA (Molar concentration) in ACN + 1 M TEABF$_4$. Platinum working and counter electrodes. Scan rate 10 mV s^{-1}, ambient temperature.

Fig. 2. Cyclic voltammograms in the anodic and cathodic regions for EA, EDFA and ClMB (Molar concentration) in ACN + 1 M TEABF$_4$. Platinum working and counter electrodes. Scan rate 10 mV s^{-1}, ambient temperature.
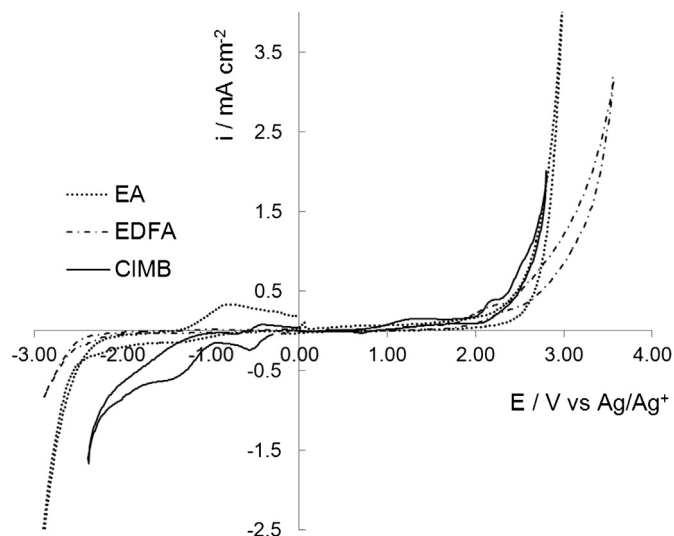
is sustained by the higher stability towards reduction of the fluorinated solvent which exhibits the same kinetic stability in reduction than EA, C–F bond being more stable compared to the C–Cl one. The incorporation of a methoxy group has no influence on the cathodic kinetic stability (Fig. 1). On the other hand, methoxy moieties deeply reduced the anodic potential window, since the oxidation of the ether function for methoxy methyl acetate (MMOA) and methoxy-2-propyl acetate (MPA) is observed at about 2 V *vs* Ag/Ag$^+$. It should be noticed that this oxidation process occurs at higher potential than for aliphatic ethers as dimethyl ether (1 V *vs* Ag/Ag$^+$) [25], presumably due to the electron withdrawing effect of the vicinal carbonyl function. The incorporation of a nitrile group decreases significantly the cathodic stability of the ester, the reduction of methyl cyanoacetate (MCA) being observed at −1 V *vs* Ag/Ag$^+$. This weak electrochemical stability is due to the acidic character of the C–H bond vicinal of two electron withdrawing functions, i.e. nitrile and carbonyl allowing to observe the H$^+$/H$_2$ redox system. The attribution of this redox process is confirmed by using a carbon working electrode that leads a shift towards a more negative value of this reduction step, in good agreement with hydrogen reduction which is sensitive to the electrode material surface. On the anodic side, the MCA exhibits a large kinetic stability, whereas the shape of the curve seems to point out the passivation of the electrode.

Several solvents can be selected for physico-chemical investigations, due to their high electrochemical window appropriate to EDLC application. In the case of the ester family, MMOA, EDFA and MPA were selected; the EA was studied for comparison.

3.2. Thermal properties

In order to obtain a good compromise between the viscosity and the dissolution of the ammonium salt, the ester solvents were investigated in the presence of ethylene carbonate, which exhibits high dielectric constant and viscosity. The proportion of each solvent is given in vol%. In addition to its high viscosity, one disadvantage of EC is its high melting point of 37 °C. Although the incorporation of 1 M ammonium salt allows the melting temperature to be decreased, this effect is very limited (few degrees) and remains insufficient to involve EC as an alternative solvent for EDLC.

The incorporation of a co-solvent should permit to decrease the melting temperature due to dipolar interaction whereas a weak impact on salt solubilisation and redox stability could be expected. The melting temperatures determined for the mixtures are reported in Table 2. The incorporation of MMOA in EC induces a great decrease in the mixture melting point; no crystallization of the mixture EC/MMOA (20/80) is observed down to −78 °C in our experimental conditions (cooling at a rate of 5 °C min^{-1}) and the melting temperature is observed at −48 °C. With the other solvents, a less pronounced decrease of the melting point is detected. In addition, as observed for EC, the incorporation of 1 M SBPBF$_4$ allows the melting point of the solvent mixture to be decreased (Table 2). Similar evolution is observed with all the solvent mixtures. The lowest melting temperature is obtained with the incorporation of MMOA, with a melting temperature close to −55 °C.

3.3. Conductivity of the electrolyte and dissociation of the salts

3.3.1. Conductivity

The ionic conductivities of the electrolytes are mainly governed by their viscosity and the salt dissociation. Two ammonium salts were investigated; at first the tetraethylammonium tetrafluoroborate TEABF$_4$, often used in supercapacitor application due to its high electrochemical stability and its low cost. However, this salt exhibits a poor solubility in weakly polar solvents (lower than 1 mol L^{-1}). Therefore the spiro-(1,1')-bipyrrolidinium tetrafluoroborate (SBPBF$_4$) was also investigated due to its higher solubility in many solvents. In EC, the solubility limits are 3.4 mol L^{-1} and 1.9 mol L^{-1} at 25 °C for SBPBF$_4$ and TEABF$_4$, respectively [16].

The conductivities at 30 °C of the different mixtures for the two salts are compared in Fig. 3. The conductivity of EC + 1 M TEABF$_4$ is slightly higher than for EC + SBPBF$_4$, with 20 mS cm^{-1} and 17 mS cm^{-1} at 30 °C respectively. This difference can be due to the lower viscosity value of EC + 1 M TEABF$_4$ (2.5 mPa s at 40 °C) compared to that of EC + 1 M SBPBF$_4$ (2.6 mPa s at 40 °C). For the two ammonium salts, the addition of 20% and 50% EDFA or EA permits to slightly increase the conductivity compared to pure EC based electrolytes, whereas a conductivity improvement is only observed for SBPBF$_4$ salt when MMOA is added. On the other hand,

Table 2
Melting and crystallization temperatures of the solvent mixtures and electrolytes in 50/50 vol%.

Solution	Melting temperature/°C	Crystallization temperature/°C
EC	40	17
EA	−84	−
MMOA	−48	−69
EC/EA (80/20)	37	23
EC/EA (50/50)	22/36	−9/21
EC/EA (20/80)	10	−28
EC/EDFA (80/20)	23	7
EC/EDFA (50/50)	17	−3
EC/EDFA (20/80)	1	−40
EC/MMOA (80/20)	−50/26	−3/15
EC/MMOA (50/50)	−50/11	−64/−5
EC/MMOA (20/80)	−48	−78
EC/MPA (80/20)	24	37
EC/MPA (50/50)	29	16
EC/MPA (20/80)	18	−13
EC 1 M SBPBF$_4$	35	11
EC/EA (50/50) 1 M SBPBF$_4$	10/24	8/−10
EC/EDFA (50/50) 1 M SBPBF$_4$	1	−75
EC/MMOA (50/50) 1 M SBPBF$_4$	−59/−53	−74
EC/MPA (50/50) 1 M SBPBF$_4$	−1	−57

The crystallization of the MPA and EDFA were not observed in our experimental conditions, 5 °C min^{-1} up to −100 °C.
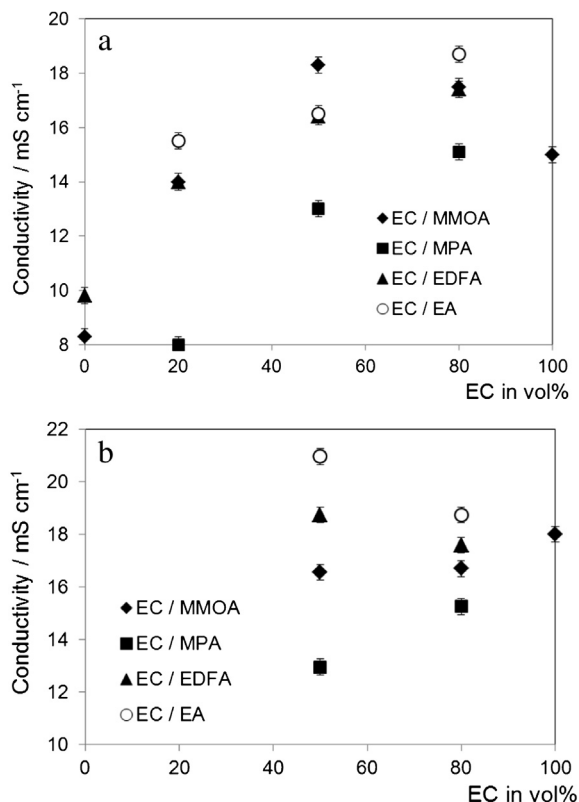
Fig. 3. Conductivity evolution, at EC/ester based electrolytes at 30 °C, versus the EC proportion in vol% electrolyte a) 1 M SBPBF$_4$, b) 1 M TEABF$_4$.

Fig. 4. Conductivity versus temperature for EC/ester (50/50 in vol %) electrolyte a) 1 M SBPBF$_4$ b) 1 M TEABF$_4$.

the addition of MPA leads to a decrease of the ionic conductivity with the two salts. Furthermore, the use of SBPBF$_4$ allows the addition of a large amount of ester co-solvent, up to 100% with MMOA and EDFA and 80% with MPA, due to its higher solubility.

The evolution of conductivities with temperature is presented in Fig. 4 for various solvent mixtures (50/50 in proportion) with 1 M for TEABF$_4$ or SBPBF$_4$ salts. For the highest temperature under study (up to 60 °C), the highest conductivity values were obtained with the mixture EC/MMOA + 1 M SBPBF$_4$, while the incorporation of ester co-solvents has no significant effect with 1 M TEABF$_4$, and the ionic conductivities are very close to those obtained with EC + 1 M TEABF$_4$. With SBPBF$_4$, the addition of 50% of MMOA improves the conductivity by a factor 1.2 at 60 °C compared to EC 1 M SBPBF$_4$, with 27 mS cm^{-1} and 22 mS cm^{-1} respectively.

The main effect of co-solvent addition is observed at low temperatures. EC + 1 M ammonium BF$_4$ electrolytes exhibit very low conductivity values below 5 °C, associated with the solidification of the electrolyte. As the solubility limits of the two salts are quite different, the conductivity drop observed at the same temperature cannot be associated with the salt precipitation and then may be associated with the electrolyte crystallization. The drop of conductivity is less pronounced with SBPBF$_4$ than with TEABF$_4$, but occurs at the same temperature. The addition of ester co-solvents induces a significant decrease of the electrolyte solidification temperature, thus the conductivity drop is observed at very low temperature. With the addition of MMOA in EC based electrolyte, the solidification occurs at −30 °C, in our experimental conditions, with SBPBF$_4$ and at lower temperature with TEABF$_4$. The crystallization of the electrolyte occurs between −10 °C and −20 °C with the addition of EDFA, MPA and EA in EC + TEABF$_4$ electrolytes, whereas with SBPBF$_4$ the conductivity decrease is observed below −25 °C. Due to its higher solubility limit, SBPBF$_4$ allows to
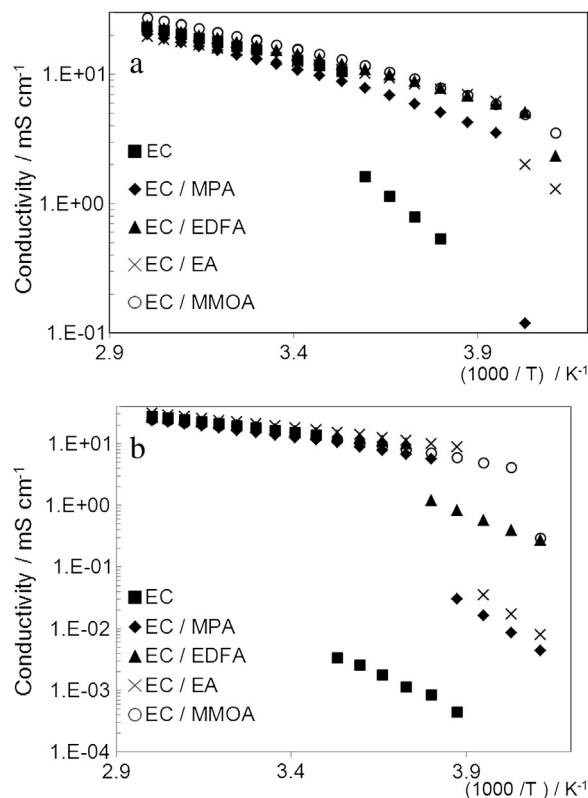
explore low temperatures, and to maintain relatively high conductivity values. This effect is remarkable at −10 °C in comparing the conductivity values of MMOA/EC (50/50) + 1 M TEABF$_4$ and 1 M SBPBF$_4$ (i.e 7 mS cm^{-1} and 8 mS cm^{-1}, respectively) while PC + 1 M TEABF$_4$ conductivity is only 4.6 mS cm^{-1}.

3.3.2. Viscosity

To evaluate the impact of both viscosity and ion dissociation on ionic conductivity, viscosity of the electrolytes was determined at 40 °C with 1 M SBPBF$_4$ (Table 3). SBPBF$_4$ was selected for this study due to its highest solubility. The mixing of ester co-solvents with EC based electrolyte induces a significant decrease in viscosity; the lowest viscosities are obtained with the addition of EA, however the viscosities obtained with the incorporation of EDFA or MMOA are slightly higher. For comparison, the viscosities of EC/MMOA + 1 M TEABF$_4$ electrolytes were measured (Table 3). The electrolyte viscosities with TEABF$_4$ and SBPBF$_4$ are equivalent, in agreement with the similar structure of the cations. In addition, viscosity and conductivity can be used to evaluate the salt dissociation in the different electrolytes through the Walden rule $\Lambda * \eta = k$ where Λ is the molar conductivity and η is the viscosity; k is a temperature dependent constant. The Walden rule was originally based on observations of the properties of dilute aqueous solutions, but has since been found to be applicable in non-aqueous electrolyte solutions [26] and molten salts [27].

Thus the evolution of the product $\eta * \Lambda$ with the electrolyte composition is associated with a modification of the salt dissociation with the solvent mixture composition. As expected, Fig. 5 shows that the incorporation of an ester in EC based electrolyte decreases the salt dissociation. Indeed, the ester solvents under study have a dielectric constant between 6 and approximately 8 which is much lower than EC one ($\varepsilon_r = 90$). Indeed, the addition of a methoxy or a fluorinated group may induce a moderate/small

Table 3
Viscosity of the electrolytes at 40 °C, with 1 M SBPBF$_4$ 1 M and 1 M TEABF$_4$.

Electrolyte mixture	η/mPa s at 40 °C				
Proportion EC in vol%	100	80	50	20	0
SBPBF$_4$					
EC/MMOA	2.6	2.25	1.9	1.56	1.51
EC/EA	2.6	2	1.18	1.24	–
EC/EDFA	2.6	2.23	1.84	1.36	1.15
EC/MPA	2.6	2.5	2.43	2.18	–
TEABF$_4$					
EC/MMOA	2.5	2.28	1.92	–	–

increase of the dielectric constant compared to those of EA ($\varepsilon_r = 6$). The effect of the co-solvent nature on the salt dissociation is significant from 50% of co-solvent. At this proportion, the incorporation of ester solvent with a supplementary functionality has a weaker effect on the dissociation decrease than EA, in accordance with the higher dielectric constant. For a higher proportion of co-solvent i.e. 80%, the best salt dissociation is obtained with MMOA, which explains the good conductivities obtained with this co-solvent despite its higher viscosity value ($\eta = 0.82$ mPa s^{-1}) compared to EDFA ($\eta = 0.65$ mPa s^{-1}) and EA ($\eta = 0.34$ mPa s^{-1}). The difference of the salt nature was evaluated in EC/MMOA based electrolytes. The product $\eta * \Lambda$ is close for the two salts, for both EC electrolyte and EC/MMOA ones. A weak increase of the product $\eta * \Lambda$ is observed with SBPBF$_4$ in EC/MMOA (50/50) compared to TEABF$_4$ based electrolyte which may be associated to a weak improvement of the salt dissociation.

3.3.3. Self-diffusion coefficient

As TEABF$_4$ and SBPBF$_4$ based electrolytes exhibit similar conductivity and viscosity and MMOA is the most promising co-solvent, NMR investigation was performed only on EC/MMOA + 1 M TEABF$_4$ electrolyte. This study was performed to extend the results obtained from the quantitative (phenomenological/macroscopic) Walden approach with a molecular approach.

If the electrolytes are totally dissociated (free ions), the molar conductivity of the electrolyte, Λ_{NMR}, can be estimated from the self-diffusion coefficients using the Nernst–Einstein equation.

$$\Lambda_{NMR} = \frac{N_A e^2 (D^+ + D^-)}{kT}$$

where D^+ and D^- are the diffusion coefficients of cation and anion (as determined by Pulsed field gradient NMR), N_A is the Avogadro

Fig. 5. Evolution of the Walden product versus the EC (in vol%) for ◇ EC/MMOA SBPBF$_4$, □ EC/MPA SBPBF$_4$, × EC/EDFA SBPBF$_4$, ˙ EC/EA SBPBF$_4$, ▲ EC/MMOA TEABF$_4$.

number, e is the electric charge on each ionic carrier, k is the Boltzmann constant and T the temperature.

However, the diffusion coefficient determined by NMR relates to all the species inside the liquid, i.e. isolated, ion-pair and also larger aggregates whereas the conductivity measurements reflect exclusively the mobility of the charged species. Thus, the Nernst–Einstein equation allows the dissociation ratio to be determined. Generally, due to ionic association, the calculation of molar conductivity from NMR diffusion coefficients overestimates the conductivity values with respect to the experimental ones (Λ_{imp}) determined by impedance measurement. The ratio between the experimental conductivity, Λ_{imp}, and the molar conductivity calculated from NMR, Λ_{NMR}, corresponds to the dissociation degree, $\alpha = \Lambda_{imp}/\Lambda_{NMR}$ The cationic transference number, T^+, was determined using the anion and cation diffusion coefficients. The results obtained are given in Table 4. In agreement with the viscosity decrease, the mobility (self-diffusion) of ions and solvents increases with the addition of MMOA. In EC electrolyte, the mobility of the BF$_4^-$ anion is slightly higher than for the TEA$^+$ cation. The bare ionic radii are equal to 0.48 nm and 0.67 nm for BF$_4^-$ and TEA$^+$, respectively [28], and 1.4 and 1.35 nm as solvated from PC [29]. The ion mobility obtained in EC seems to be well associated with the solvated ion sizes which are very close. An increase of the cationic transference number is obtained with the addition of MMOA (i.e. $T^+ = 0.44$ (EC/MMOA (50/50 in vol%)) instead of $T^+ = 0.40$). This T^+ increase could be due to a larger coordination solvation of the BF$_4^-$ anion in presence of MMOA, indeed the solvation shell depends on the solvent nature [29,30] or a lower dissociation of the salt in MMOA + EC mixture. This second hypothesis is presumably more satisfactory since MMOA leads to the decrease of the overall polarity of the mixture resulting in a higher tendency for ion pair formation. The α values are less than unity indicating that not all the diffusive species contribute to the ionic conduction, i.e. presence of free-ion, ionic pair or/and cluster. A decrease of the values, i.e. a decrease of the proportion of free ion is observed with the addition MMOA in agreement with its lower dielectric constant (close to 8 compared to 90 for EC). The dissociation decrease measured by NMR is in good accordance with the data obtained using the Walden plot. The ion dissociation, measured by NMR, is 20% lower in EC/MMOA (50/50) than in EC electrolyte whereas the qualitative approach of the Walden plot leads to 29%.

The EC/MMOA (50/50) + 1 M ammonium salt electrolytes exhibit a good compromise between viscosity and dissociation. A conductivity improvement is obtained compared to PC + TEABF$_4$, EC/MMOA (50/50) electrolytes with both TEABF$_4$ and SBPBF$_4$ 1 M exhibit conductivities of 16.6 and 18.3 mS cm^{-1}, respectively compared to 14 mS cm^{-1} for PC + 1 M TEABF$_4$ at 30 °C.

3.4. Electrochemical study in EDLC configuration

Due to their high conductivity values, particularly at low temperature, EC/MMOA and EC/EDFA + 1 M TEABF$_4$ electrolytes have been evaluated in supercapacitor configuration. The cyclic voltammetry (CV) curves for EDLCs based on these electrolytes are presented in Fig. 6 (scanning rate of 100 mV s^{-1}) and compared to ACN and EC/EA based electrolytes. The CVs exhibit a rectangular box shape, associated with a purely capacitive behaviour [31]. The small distortion observed at high voltage with EC/MMOA and EC/EDFA electrolytes is associated with the internal resistance which is higher for EC based electrolytes than for the ACN one. The distortion is however lower than that observed with PC + tetraethylammonium BF$_4$ 1 M [7]. CVs were performed at a low scan rate, 1 mV s with different voltage ranges in order to evaluate the electrochemical stability of the ester based electrolytes (Fig. 7). Up to 2.5 V, no faradic process is observed for the
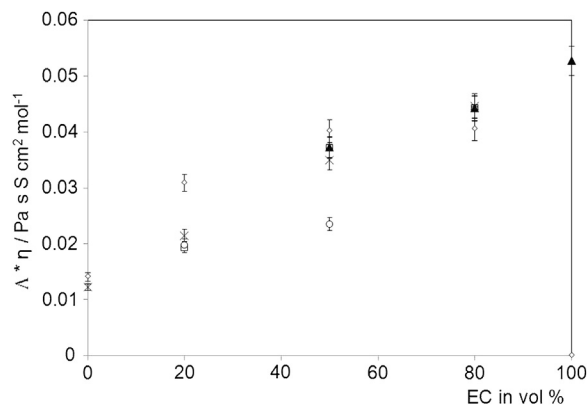
Table 4
PFG NMR diffusion coefficients of the anion, cation, cationic transference number, T^+ (from NMR measurement) and dissociation degree, $\alpha = \Lambda_{imp}/\Lambda_{NMR}$, of EC/MMOA + 1 M TEABF$_4$ electrolytes. The self-diffusion coefficient values are given with an accuracy of less than 5% ($T = 40\ °C$).

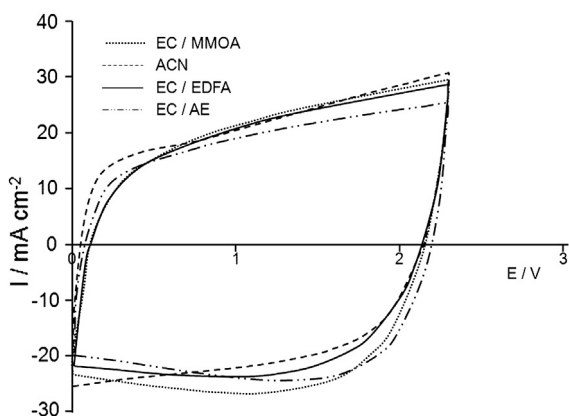| Electrolyte	$D_{TEA+}/10^6$ cm^2 s^{-1}	$D_{BF4-}/10^6$ cm^2 s^{-1}	$D_{EC}/10^6$ cm^2 s^{-1}	$D_{MMOA}/10^6$ cm^2 s^{-1}	T^+	σ_{imp} at 40 °C/mS cm^{-1}	α
EC	3.94	5.90	6.31	–	0.40	21.1	0.60
80 EC + 20 MMOA	4.46	6.32	7.24	7	0.41	19.4	0.51
50 EC + 50 MMOA	5.09	6.56	8.42	8.4	0.44	19.4	0.47

Fig. 6. Cyclic voltammograms of the different electrolytes at 100 mV s^{-1} in 1 M TEABF$_4$ based electrolyte.

ester based electrolytes. The EC/MMOA 1 M TEABF$_4$ electrolyte points out faradic process for a potential window higher than 2.8 V, in accordance with its lowest electrochemical stability observed on platinum electrode (Fig. 1) than EA and EDFA based electrolytes. The capacitance, the internal resistance and the time constant were determined for the cell studied and are given in Table 5. The capacitance values obtained with the different electrolytes are close. The use of SBPBF$_4$ instead of TEABF$_4$ has no effect on the internal resistance but slightly improves the capacitance values for all the electrolytes studied. A good cyclability is observed, with only a capacitance loss between 1% and 3% after 1500 cycles (as measured between the 100th and the 1600th cycles) for both EC + ester 1 M TEABF$_4$ and 1 M SBPBF$_4$ electrolytes. A higher stability is obtained with SBPBF$_4$ salt, with a capacitance loss between 1% and 2%. The EC/EA based electrolytes present the lowest stability with a loss of 3% and 1.2% with TEABF$_4$ and SBPBF$_4$, respectively. Using the same experimental conditions, a capacitance loss of 2% is obtained with ACN based electrolytes. Due to the difference in conductivity values, the internal resistance is higher for EC + ester electrolytes than ACN ones. However, the
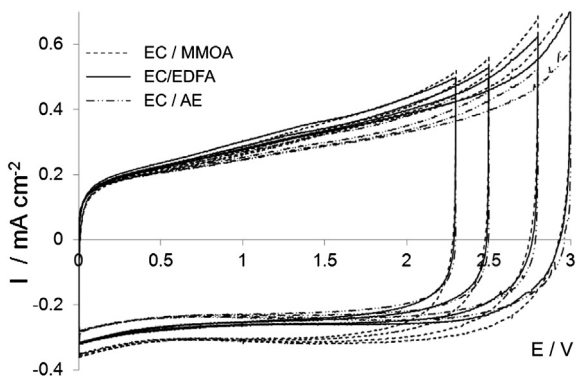
Table 5
Capacitance (C), internal resistance (R) and time constant (τ) of the EDLC performed using different electrolytes.

	C/mF cm^{-2}	R/Ω cm^{-2}	τ/s
ACN + 1 M TEABF$_4$	312	2.5	0.8
ACN + 1 M SBPBF$_4$	320	2.6	0.8
EC + MMOA (50/50) + 1 M TEABF$_4$	320	7.1	2.3
EC + MMOA (50/50) + 1 M SBPBF$_4$	325	7	2.3
EC + EDFA (50/50) + 1 M TEABF$_4$	310	7	2.2
EC + EDFA (50/50) + 1 M SBPBF$_4$	325	7	2.3
EC + EA (50/50) + 1 M TEABF$_4$	305	6.7	2.05
EC + EA (50/50) + 1 M SBPBF$_4$	330	6	2
EC + 1 M SBPBF$_4$	275	54	15

addition of MMOA or EDFA induces the same performances than EA with a much more secure co-solvent.

4. Conclusion

The incorporation of ester co-solvents in ethylene carbonate based electrolytes has been studied. Ester solvents with methoxy or fluorine groups exhibit high electrochemical kinetic stability, and interesting physico-chemistry properties. Moreover, the good compromise between low viscosity and high ion dissociation allows conductivity higher than 18 mS cm^{-1} at 30 °C to be exhibited. The best co-solvents are MMOA and EDFA, which give the similar performances compared to EA with a large improvement of the safety issue. Performances higher than those obtained with PC based electrolyte are obtained. The conductivity at low temperature is enhanced by the use of SBPBF$_4$ due to its higher solubility. The cycle life of the system is improved using SBPBF$_4$ instead of TEABF$_4$ and a good cyclability was obtained during 1500 cycles with an operating voltage of 2.3 V.

Acknowledgements

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Fig. 7. Cyclic voltammograms, with different voltage ranges, of the different electrolytes at 1 mV s^{-1} in 1 M TEABF$_4$ based electrolyte.

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